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Molecular braids: quintuple helical hydrogen bonded molecular network†

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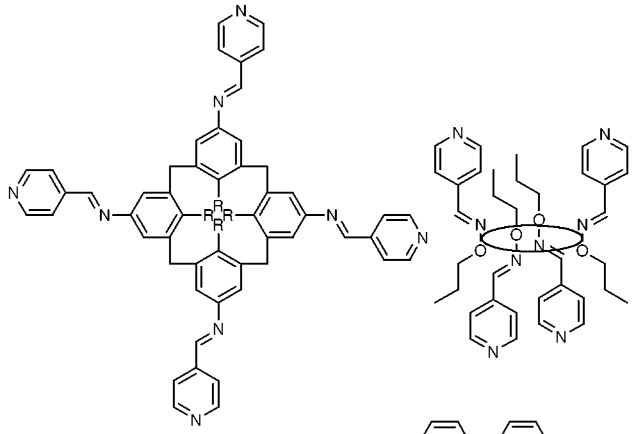
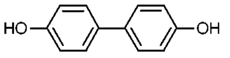
The synthesis of 1, characterized by a calix[4]arene backbone in 1,3-alternate conformation bearing four pyridines acting as hydrogen bond acceptors, was achieved and its solid state structure studied by X-ray diffraction on a single crystal; in the presence of 4,4′-biphenol 6 acting as a dihydrogen bond donor, compound 1 formed infinite single strand helical 1-D molecular networks which upon lateral association were packed in the crystalline phase as quintuple helices.

Molecular networks are formed by molecules possessing complementary interaction sites oriented in a divergent mode. One may tune the dimensionality (1-, 2- or 3-D) and the topology of molecular networks through the interplay between complementary components. Recently, much effort has been invested in obtaining a variety of molecular networks such as inclusion,[1] hydrogen bonded[2] or coordination networks.[3] Concerning 1-D networks, the formation of helical assemblies is a subject of current interest[4,5] and the understanding of lateral interactions between helical 1-D networks remains a challenge. Examples of helical arrangements in a variety of supramolecular assemblies have been reported.[6–8]

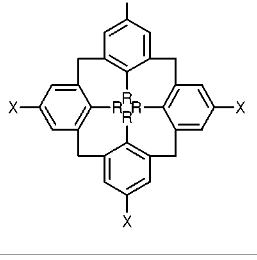
Here, we report the synthesis of a new building block **1** characterized by a calix[4]arene backbone in 1,3-alternate conformation and bearing four pyridine groups as hydrogen bond acceptors, as well as the structural analysis of the free ligand and of its helical hydrogen bonded molecular network obtained in the presence of 4,4′-biphenol **6**.



1 R = O(CH$_2$)$_2$Me



6



2 X = Bu^t, R = OH
3 X = Bu^t, R = O(CH$_2$)$_2$Me
4 X = NO$_2$, R = O(CH$_2$)$_2$Me
5 X = NH$_2$, R = O(CH$_2$)$_2$Me

We have been interested in the formation of molecular networks using both H-bonds and electrostatic charge–charge interactions.[9] Molecular units possessing four H-bond acceptor sites occupying the apices of a pseudo-tetrahedron may be used for the formation of helical networks in the presence of H-bond donors possessing two divergently oriented polarised hydrogen atoms. The design of such a tecton may be based on a preorganised moiety such as a calix[4]arene backbone which offers the possibility of anchoring four H-bond acceptors in an alternating mode below and above its main plane. This type of unit is obtained using both the upper- and lower-rims of calix[4]arene. By transforming all four OH into OPr groups, the 1,3-alternate conformation was imposed, whereas by amination of the upper rim, four pyridines as H-bond acceptor groups were introduced through imine junctions. The choice of the imine functionality in *E* configuration connecting pyridines to the calix unit was based on the design of **1** which requires that pyridines should be oriented perpendicularly to the main plane defined by four CH$_2$ groups of the calix. Using the above mentioned strategy, calix[4]arene derivatives in 1,3-alternate conformation bearing catechol[10] or four nitrile groups[11] have been reported. An analogue of compound **1** with the calix unit in cone conformation was previously prepared.[12]

Dealing with the hydrogen bond donor part, 4,4′-biphenol **6** which possesses two phenolic groups oriented in a divergent mode and thus capable of forming an infinite hydrogen bonded molecular network was chosen.

Starting with **2**,[13] its tetra-alkylation with PrI in refluxing benzene and in the presence of Bu^{t}OK produced the desired compound **3** after crystallisation.[14] The latter, upon *ipso-*

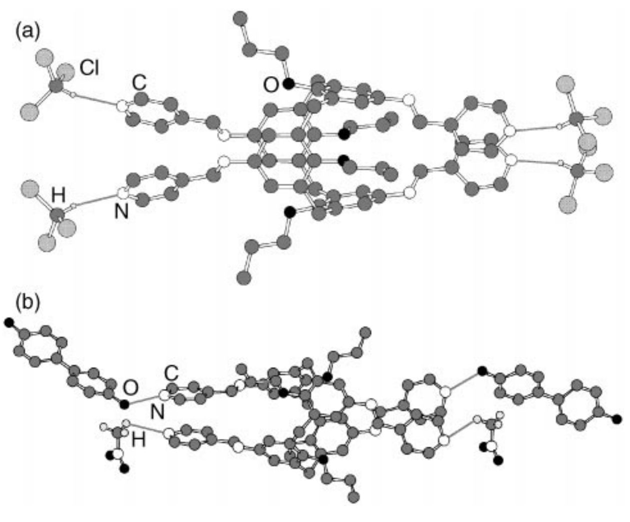


Fig. 1 (a) X-Ray structure of **1**. H atoms except for CHCl$_3$ are omitted for clarity; (b) a portion of the X-ray structure of $(\mathbf{1}\cdot\mathbf{6})_n$ H-bonded network showing the surroundings of **1** and **6**. H atoms except for MeNO$_2$ are omitted for clarity.

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† Dedicated to Jean-Marie Lehn on the occasion of his 60th birthday.

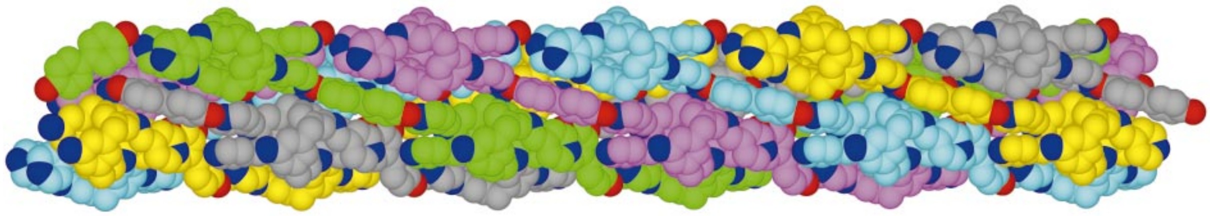

Fig. 2 A portion of the X-ray structure of $(\mathbf{1}\cdot\mathbf{6})_n$ hydrogen bonded network showing the formation of a quintuple helical arrangement comprised of five right handed helical strands represented in different colours for clarity. H atoms, $O(CH_2)_2Me$ groups and $MeNO_2$ molecules are not shown (for distances and angles see text).

nitration,[14] gave the tetra-nitro compound **4** which was reduced to the amino compound **5** using $SnCl_2$ in EtOH.[10] Finally, treatment of **5** with 4.2 equiv. of 4-pyridylcarbaldehyde in EtOH at 80 °C in the presence of a catalytic amount of AcOH for 12 h afforded compound **1** in 52% yield after crystallisation from $CHCl_3$–MeOH.

The structure of **1** was confirmed by X-ray diffraction on a single-crystal obtained upon cooling from 80 to 25 °C a mixture of $MeNO_2$ (2 ml) and $CHCl_3$ (1 ml) containing compound **1** (2 mg).‡ As expected, compound **1** adopts a slightly pinched 1,3-alternate conformation [Fig. 1(a)]. The imine groups are in *E* configuration with an average C=N distance of 1.256 Å and C–N=C and C–N=C–C dihedral angles of 117.5 and 172.2° and −172.2° respectively. Interestingly all four pyridine units are hydrogen bonded to a $CHCl_3$ molecule with $C\cdots N$ and $N\cdots H$ distances of 3.233 and 2.338 Å respectively and an NHC angle of 156.8° demonstrating the H-bond acceptor feature of the pyridine units.

Upon slow cooling of a $MeNO_2$ (3 ml) solution of **1** (2 mg) and **6** (1.6 mg) from 80 °C to room temp., single crystals were obtained. X-Ray diffraction‡ revealed the formation of a network composed of **1**, **6** and $MeNO_2$ molecules in 1:1:1 ratio. The H-bond acceptor **1** and donor **6** form by mutual bridging a single stranded helical network which crystallises in the non-centric space group $P4_1$ or $P4_3$ [Fig. 1(b)]. The reason for the spontaneous chiral separation remains unclear. The pitch of the helix which extends along the *z* axis is composed of four **1**, four **6** and four $MeNO_2$. For each calix unit, among the four pyridines present, two of them, located on opposite sides of the backbone, participate in the formation of a helical arrangement through strong H-bonds with $N\cdots O$ distances of 2.703 and 2.776 Å. For the remaining two pyridines, each is located in close proximity to one $MeNO_2$ molecule with $C\cdots N$ distances of 3.290 and 3.312 Å. The observed helical structure is derived from the primary structure of ligand **1** which possess a S_4 screw axis. Rather interestingly, probably for best compacting reasons, five helical strands of the same handedness associate laterally in a helical fashion leading to a quintuple helical braid (Fig. 2). The formation of the braided arrangement is probably due to the uncharged nature of **1** and **6** as well as edge-to-face interactions between the pyridine units of **1** and the phenyl groups of **6** which operate in conjunction with van der Waals interactions. Finally, the quintuple helices associate laterally to form the crystal.

In conclusion, using a tetra-H-bond acceptor possessing an S_4 screw axis and a divergently oriented di-H-bond donor, a quintuple helical arrangement was obtained in the crystalline phase. The formation of the supramolecular assembly may be described as the result of molecular organisation at three different levels. The formation of a single stranded H-bonded helical network (first level), the formation of the quintuple helical braided network (second level) and the lateral association of braided networks into the compacted solid (third level). The role of the H-bond donor length and the thickness of H-bond acceptor on the pitch as well as the number of braided strands is currently under investigation.

Notes and references

‡ *Crystallographic data*: for **1** (yellow crystals, 173 K): $C_{64}H_{64}N_8O_4\cdot 4CHCl_3$, M = 1486.79, tetragonal, space group $I4_1/a$, a = 17.3435(6), b = 17.3435(6), c = 24.104(1) Å, U = 7250.4(9) Å^3, Z = 4, D_c = 1.36 g cm^{-3}, Mo-Kα graphite monochromated radiation, kappaCCD, μ = 0.510 mm^{-1}, 2474 data with $I > 3\sigma(I)$, R = 0.067, R_w = 0.079.

For $(\mathbf{1}\cdot\mathbf{6})_n$ (colourless crystals, 173 K): $C_{64}H_{64}N_8O_4\cdot C_{12}H_{10}O_2\cdot CH_3NO_2$, M = 1256.53, tetragonal, space group $P4_1$ or $P4_3$, a = 17.208(1), c = 23.775(1) Å, U = 7039(1) Å^3, Z = 4, D_c = 1.19 g cm^{-3}, Mo-Kα graphite monochromated radiation, KappaCCD, μ = 0.078 mm^{-1}. The diffraction power of the crystal was rather poor, only 2057 reflections out of 10545 had $I > 3\sigma(I)$. Therefore, all atoms were kept with isotropic temperature factors and 2724 data with $I > 2\sigma(I)$ were used for refinements. Attempts to determine the absolute configuration using the Friedel's pair method failed. R = 0.099, R_w = 0.120. CCDC 182/1427. See http://www.rsc.org/suppdata/cc/1999/xxxx/ for crystallogrpahic files in .cif format.

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